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## RESONANT CARS SPECTROSCOPY OF *s*-TETRAZINE VAPOUR

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CARS experiments on *s*-tetrazine vapour show that the electronic resonance enhancement in the Q-branch is most effective for the lower *J* values. This suggests that the radiationless relaxation rate in the excited state increases with rotational quantum number. Delayed picosecond CARS experiments indicate that the rotation-vibration coupling for the 1008 cm<sup>-1</sup> ground-state vibrational mode is approximately 2 MHz.

### 1. Introduction

Coherent anti-Stokes Raman scattering (CARS) has been shown to hold great potential as a new technique in the study of photochemical reactions [1].

We have been involved with time-resolved picosecond CARS experiments on *s*-tetrazine vapour aimed at a better understanding of the photochemistry of this molecule [2-6]. The initial goal was to probe in the gas phase, the time-resolved photochemical production of N<sub>2</sub>, which, next to HCN, is one of the reaction products [7]. In the course of our experiments it became clear however, that, with the laser peak powers used, the CARS detection sensitivity for nitrogen was too low. Fortunately, some interesting effects in the electronically enhanced CARS excitation spectrum of the 1008 cm<sup>-1</sup> vibration and in the time-resolved coherent decay of this mode were observed.

In this letter we present results which show that the maximum of the electronically enhanced CARS excitation spectrum of the 1008 cm<sup>-1</sup> mode is not at the top of the Q-branch, but at the sharp edge. A possible interpretation is that the photochemical reaction rate increases with increasing rotational quantum number. A second interesting feature is the observation of a long-lived free induction decay CARS signal. From the Fourier transform of this signal combined with informa-

tion on the resonance enhancement in the Q-branch of the electronic origin, we calculate the rotation-vibration coupling constant in the 1008 cm<sup>-1</sup> mode to be 1.9 MHz.

### 2. Experimental

In the resonant CARS excitation experiment two nitrogen-pumped dye lasers were used. One of the dye lasers (Molelectron DL-200) operating around 5515 Å employed coumarin 495 in ethanol as the lasing medium and was pumped by a Molelectron UV-12 nitrogen laser. The second dye laser, home-built was centered at 5840 Å, used rhodamine 6G in ethanol as lasing medium and was pumped by a Molelectron UV-400 nitrogen laser. Both dye lasers produced 5 ns pulses with peak powers between 5 and 10 kW and had a bandwidth of about 0.5 cm<sup>-1</sup>. The time coincident laser pulses were combined via a beam splitter or direct vision prism and focused into a glass cell of 36 cm length, using a 20 cm focal-length lens. The CARS signal was separated from the excitation beams with a direct vision prism and detected, via a Spex 1704 monochromator with a photomultiplier type EMI 9816. The signal was further processed via a boxcar, PAR model 162 with digital storage option.

In the ps free-induction decay CARS experiment, amplified ps pulses of two synchronously pumped dye lasers were used. The characteristics and operation of

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this system have been described in a previous paper [8]. In the decay experiments reported here, nearly transform-limited pulses of  $\approx 20$  ps were used ( $\approx 1$  cm $^{-1}$ ). Occasionally, longer pulses of about 100 ps were generated by sticking additional etalons (flat quartz plates) in the dye-laser cavities.

The delayed probe pulse was crossed at an angle of  $\approx 1.5^\circ$  with the excitation pulses. The delayed CARS signal, because of the phase-match condition spatially tracking the delayed probe pulse, was detected as described earlier in this section.

s-tetrazine, synthesized as described by Spencer et al. [9], was kept cold and in the dark until used. The s-tetrazine pressure in the glass cell was varied by cooling of a side arm of the cell. The actual s-tetrazine pressure was measured with a capacitance manometer.

### 3. Results and discussion

#### 3.1. Resonant CARS excitation spectrum

Fig. 1 shows the CARS excitation spectrum for the 1008 cm $^{-1}$  mode and the absorption spectrum (squared) of the Q-branch of the electronic origin of s-tetrazine at 5515 Å. The s-tetrazine vapour pressure was  $(2.5 \pm 0.5) \times 10^{-3}$  Torr.

The CARS excitation spectrum was taken in the following way. One of the dye lasers was set at a point in the Q-branch, while the other was tuned around the 1008 cm $^{-1}$  vibrational resonance for maximal CARS signal. This process was repeated for numerous points in the Q-branch leading to the CARS excitation spectrum of fig. 1. At each point the wavelength of both lasers was accurately measured using a 1 m Spex 1704 and an iron arc for calibration. The maximal CARS signal was always measured at a frequency difference between the lasers of 1008 cm $^{-1}$ . We note that in solid s-tetrazine this vibration ( $\nu_1$ ) is observed at 1017 cm $^{-1}$  and is the most intense in the Raman spectrum [10]. Two things are noteworthy in the spectrum of fig. 1. The first is that the maximum CARS enhancement is *not* at the absorption maximum but at the sharp band edge. Accurate measurements show that the maximum occurs at  $18132.1 \pm 0.6$  (vac) cm $^{-1}$  which is near the reported Q-band head of  $18132.7 \pm 0.1$  (vac) cm $^{-1}$  [11]. A second interesting feature concerns the width of the CARS enhancement which is significantly less than the

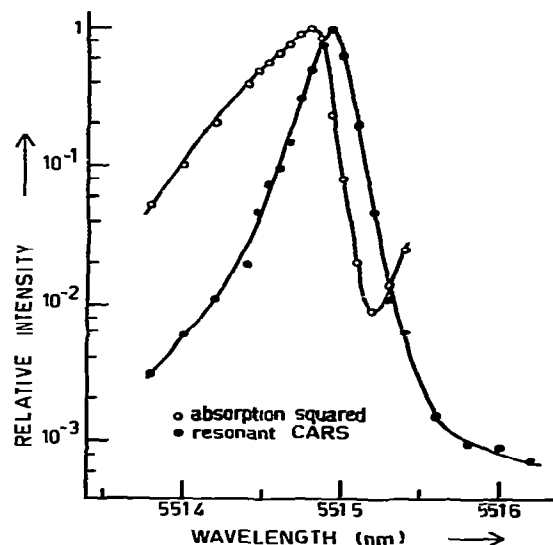


Fig. 1. Absorption spectrum squared (o) and CARS excitation spectrum (•) of the Q-branch of the electronic origin of s-tetrazine at 5515 Å. In the CARS excitation experiment the frequency difference between the laser and Stokes pulses was fixed at 1008 cm $^{-1}$ .

width of the squared Q-branch absorption. In a separate experiment, employing bandwidth-limited 100 ps pulses ( $\approx 4$  GHz), the CARS enhancement width (fwhm) was determined to be  $12.5 \pm 2.5$  GHz compared to a 30 GHz width of the Q-branch squared absorption. Druet et al. [12] recently considered in great detail the effect of electronic resonance enhancement in CARS. In the case of both a vibrational and electronic resonance the non-resonant part of  $\chi^{(3)}(\chi_{NR}^{(3)})$  may be ignored and the resonance part for a specific ( $J, K$ ) level takes the form:

$$\begin{aligned} \chi_R(J, K) \propto & \rho_{JK, JK} (\omega_{21, JK} - \omega_L - i\Gamma_{21, JK})^{-1} \\ & \times [\omega_{31, JK} - (\omega_L - \omega_S) - i\Gamma_{31, JK}]^{-1} \\ & \times (\omega_{41, JK} - \omega_{AS} - i\Gamma_{41, JK})^{-1} \\ & \times S(J_1, J_2, J_3, J_4), \end{aligned} \quad (1)$$

where  $\rho_{JK, JK}$  is the population of state  $|JK\rangle$  in the electronic ground state. Note that the absorption intensity originating from  $|JK\rangle$  is proportional to  $\rho_{JK, JK} S(J_1, J_2)$  where  $S(J_1, J_2)$  is the Q-branch rotational factor [13].

In eq. (1),  $\omega_{31, JK}$  and  $\Gamma_{31, JK}$  are the Raman fre-

quency and linewidth, while  $\omega_{21,JK}$  and  $\Gamma_{21,JK}$  are the corresponding quantities for the electronic (Q-branch) transition. The parameters  $\omega_{41,JK}$  and  $\Gamma_{41,JK}$  refer to the frequency and linewidth of a vibronic transition that is near-resonant with the CARS frequency ( $\omega_{AS}$ ). Finally  $\omega_L$  and  $\omega_S$  are the laser and Stokes frequency and  $S(J_1, J_2, J_3, J_4)$  a rotational factor [14]. Assuming *s*-tetrazine to be a planar oblate symmetric top (vide infra) we have calculated the absorption and resonant CARS excitation spectrum of *s*-tetrazine [15]. In the calculation of the CARS spectrum it was further assumed that the anti-Stokes resonant contribution in eq. (1) to the CARS intensity is (*JK*) independent. Computer simulation of these spectra shows that, in the case of a (*JK*)-independent Raman and electronic transition linewidth, the resonant CARS excitation spectrum ( $\omega_{21,JK} = \omega_L$  and  $\omega_{31,JK} = \omega_L - \omega_S$ ) should follow the square of the absorption spectrum. Fig. 1 clearly shows that this expectation for resonant excitation in the Q-branch of *s*-tetrazine is not realized.

An attractive explanation for the observed discrepancy relies on the assumption that the homogeneous linewidth of the electronic transition increases with increasing rotational quantum number. As the homogeneous linewidth of the electronic transition in *s*-tetrazine is determined by a radiationless process [2] (internal conversion or photo-isomerization or dissociation) this assumption leads to the conclusion that the radiationless process becomes more efficient as the molecule rotates faster. This would imply a decrease in fluorescence lifetime with increasing *J* for excitation in the Q-branch. Langelaar et al. [16] measured the fluorescence lifetime of the excited state to be 870 ps by excitation in the Q-branch. They used short pulses ( $\approx 10$  ps) for excitation, which means that the whole Q-branch was excited. These measurements should be repeated using longer transform-limited pulses ( $\approx 250$  ps). Vemulapalli and Cassen [17] previously reported a difference in fluorescence yield for excitation in the P- and R-branch versus excitation in the Q-branch of *s*-tetrazine. This result however was not confirmed by Meyling et al. [2].

Novak and Rice [18] have shown that a *K*-dependent radiationless relaxation rate may be induced by intermanifold Coriolis coupling. If the above interpretation is correct, *s*-tetrazine presents a clear example of this theory. Further experiments on *s*-tetrazine therefore seem necessary.

### 3.2. Delayed resonant CARS

In recent years delayed CARS has been used to probe the vibrational dynamics of a variety of molecules. In a recent review [19] all aspects of the technique are discussed in great detail. Briefly, with two excitation pulses a coherent superposition of the ground state and a specific ground-state vibrational level is excited. A delayed pulse then probes the remaining *macroscopic* coherence by stimulating a delayed CARS signal. If the Raman transition is homogeneously broadened the decay of the amplitude of the CARS signal is the Fourier transform of the homogeneous linewidth. For an inhomogeneously broadened Raman transition the delayed CARS samples the frequency distribution of participating molecules. In the delayed resonant-CARS experiment on *s*-tetrazine vapour, the exciting pulses create a coherent superposition between a variety of corresponding *J* and *K* levels in the ground state and in the  $1008\text{ cm}^{-1}$  mode. If the rotation-vibration coupling were zero, the Q-branch of the  $1008\text{ cm}^{-1}$  Raman transition would collapse into a single line. In that case, in a low-pressure gas, the delayed CARS signal would only decay through the Q-branch Doppler-induced linewidth. The Doppler linewidth of the  $1008\text{ cm}^{-1}$  Raman transition is calculated to be 41 MHz. Alternatively if the Q-branch linewidth is dominated by the rotation-vibration coupling, the delayed CARS would probe the "inhomogeneous" broadening due to this effect. Fig. 2 shows the decay of the resonant delayed CARS together with the cross-correlation between the excitation pulses. It is obvious that the decay is much shorter than expected from the Doppler effect or collisional broadening at the *s*-tetrazine pressure ( $\approx 10^{-2}$  Torr) used. The apparent build-up of the delayed CARS signal we ascribe to the "slow" response of the system towards excitation. In fact the delayed CARS pulse was measured to have a width  $< 0.5\text{ cm}^{-1}$ , which for a gaussian linewidth corresponds to a response time (decay of the coherence amplitude) of  $> 60$  ps. The solid line in fig. 2 is a fit to the delayed CARS signal, assuming that the Raman transition exhibits a gaussian spectral profile with a linewidth (fwhm) of 0.94 GHz. In order to extract from the "Raman spectrum" information on the rotation-vibration coupling we have to consider in more detail the rotational structure of the *s*-tetrazine electronic and Raman transitions. From the spectroscopic work of Smalley et al. [20] on

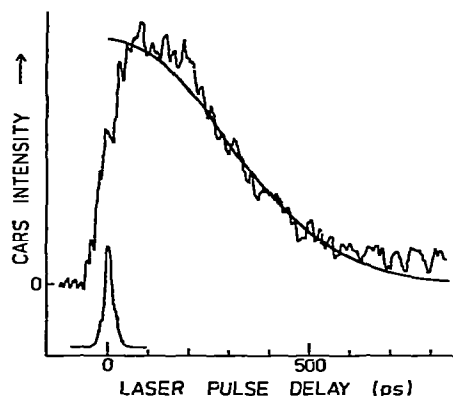


Fig. 2. Delayed resonant CARS signal of *s*-tetrazine vapour. The solid line is a fit to a gaussian decay  $[\exp(-k^2 t^2)]$  with  $k^{-1} = 400$  ps. Also shown is the cross-correlation between the laser (at 5515 Å) and Stokes (at 5840 Å) pulses, determining the point of zero delay.

*s*-tetrazine in a supersonic jet we know that to a good approximation it may be considered a planar oblate symmetric top. The energy levels of such a rotor are given by

$$E_{e,v}(J, K) = B_{e,v}J(J+1) - \frac{1}{2}B_{e,v}K^2, \quad (2)$$

where  $B_{e,v}$  is the in-plane rotational constant dependent upon electronic (e) and vibrational (v) excitation. Smalley et al. [20] determined this constant for the ground state of *s*-tetrazine to be  $B_1 = 0.2185$  cm<sup>-1</sup>, and in the excited state  $B_2 = 0.2197$  cm<sup>-1</sup>.

Realizing that in the resonant CARS experiment involving the Q-branch, the selection rules  $\Delta J = \Delta K = 0$  hold, a good estimate of the rotational constant in the 1008 cm<sup>-1</sup> mode ( $B_3$ ) should be obtainable by comparing the linewidth of the Fourier transform of the delayed CARS with the width of the resonant CARS excitation spectrum in fig. 1. From the ratio of these widths ( $\approx 19$ ) we deduce that  $|B_3 - B_1| = 1.9$  MHz. On physical grounds we assume that the larger possible value of  $B_3$  is the correct one. The rotation-vibration coupling constant for this particular mode then becomes  $\approx 1.9$  MHz. In conclusion we note that a similar delayed (off-resonant) CARS experiment on the corresponding mode (992 cm<sup>-1</sup>) in benzene in the gas phase showed that the rotational-vibrational coupling is much larger. The delayed CARS signal in this case showed a decay with a time constant of  $\approx 24$  ps. Detailed information

on the rotation-vibration coupling in these molecules could of course be obtained from cw CARS spectroscopy [21].

#### 4. Conclusion

Resonant CARS experiments on *s*-tetrazine vapour suggest that the excited-state internal conversion (or photochemistry) strongly depends on the rotational angular momentum of the initial state. Single rotational-lifetime measurements are needed to check this idea.

Fourier-transform delayed CARS spectroscopy contains information on rotation-vibration coupling. This technique holds promise for the study of the rotational structure of short-lived species or reaction intermediates.

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